



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol. 3, No.2, pp 864-869, April-June 2011

Aniline as Corrosion Inhibitor for Zinc in Phosphoric acid.

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Abstract: The corrosion of zinc in phosphoric acid containing Aniline has been studied at different acid concentrations, inhibitor concentration and temperatures. Corrosion increases with the concentration of acid and the temperature. At constant acid concentration, the inhibition efficiency (I.E.) of aniline increases with the concentration of inhibitor. At constant inhibitor concentration, the I.E. decreases with the increase in concentration of acid. As temperature increases, percentage of inhibition decreases. The plot of log ($\theta/1-\theta$) versus log C results in a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Longmuir isotherm. Galvenostatic polarization curves show polarization of both anodes as well as cathodes. **Key words:** Corrosion, zinc, phosphoric acid, aniline.

Introduction

The problem of corrosion is of considerable importance due to increase in uses of metals and alloys. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow¹. Phosphoric acid is a major chemical product, which has uses many important especially in the production of fertilizers. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors²⁻⁴. According to Hackerman et al.⁵ the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of π - orbital of free electron on the nitrogen atom of these compounds. Lin Wang et al.⁶ has studied the corrosion inhibition of zinc in phosphoric acid solution by 2 –mercaptobenzimidazole. Sivaraju and Kannan⁷ have studied the corrosion of mild steel in 1 N phosphoric acid with plant extract. In the present work, the corrosion of zinc by phosphoric acid containing isomer of aniline has been reported.

Material and Methods

To study the corrosion of zinc in phosphoric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used.

Rectangular specimens (4.50 x 2.03 x 0.17 cm) of zinc having an area of 0.2053 dm² were taken and cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M Phosphoric acid concentration with and without inhibitor containing 230 ml test solution at 301 ± 1 K for 24 h immersion period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2 % BaCO₃ for a period of about 2 minutes ⁸. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. The mean value of weight loss was reported as mg/dm² shown in Table-1. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

To study the effect of temperature on corrosion of zinc in 0.05 M H_3PO_4 , the specimens were immersed in 230 ml of corrosive solution and corrosion rate was determined at various temperatures

like 303, 313, 323 and 333 K for an immersion period of 3 h with and without inhibitor. From the data, I.E.(in %), energy of activation (Ea), heat of adsorption (Qads), free energy of adsorption (Δ Ga), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated and shown in Table- 2.

For polarization study, metal specimens having an area of 0.0268 dm^2 were immersed in 230 ml corrosive solution without and with 80 mM inhibitor concentration in 0.01 M H₃PO₄. The test cell includes the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as Platinum electrode as an auxiliary electrode. The polarization study was made by using Potentio-Galvano-Scan (Weaving PGS 81) meter. Polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (Icorr) and the corrosion potential $(E_{corr})^9$.

Results and Discussion

The results are presented in Tables 1 to 3 and in Figures 1 to 3. To assess the effect of corrosion of zinc in phosphoric acid, aniline is added as inhibitor. I.E. has been calculated as follows:

I.E. % =
$$\frac{W_u - W_i}{W} \times 100$$
 ... (1)

Where, W_{μ} is the weight loss of metal in uninhibited acid and

W_i is the weight loss of metal in inhibited acid.

Energy of activation (Ea) has been calculated from the slope of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) (Fig.2) and also with the help of the Arrhenius equation¹⁰.

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R} [(1/T_1) - (1/T_2)] - \dots - (2)$$

where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

The value of heat of adsorption (Qads) were calculated by the following equation ¹⁰. $Q_{ads} = 2.303 \ R \ [log \ (\ \theta_2 \ / \ 1 - \theta_2 \) \ \text{-} \ log \ (\ \theta_1 \ / \ 1 - \theta_1 \)] \ x$ $[T_1 . T_2 / T_2 - T_1]$ -----(3)

where, θ_1 and θ_2 [$\theta = (Wu - Wi)/Wi$] are the fractions of the metal surface covered by the inhibitors at temperature T_1 and T_2 respectively.

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The values of the free energy of adsorption (ΔGa) were calculated with the help of the following equation

 $\log C = \log \left(\theta / 1 - \theta \right) - \log B \quad ----- \quad (4)$ Where, $\log B = -1.74 - (\Delta Ga / 2.303 \text{ RT})$ and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH_a) and entropy of adsorption (ΔS_a) are calculated using the equation. $\Delta H^{\circ}_{a} = E_{a} - RT$ ----- (5) $\Delta S^{\circ}_{a} = \Delta H - \Delta G / T$ ----- (6)

The values of the rate constant k were evaluated from the weight loss data and the values of half-life $t_{1/2}$ were calculated using following equation. ----- (7)

 $t_{1/2} = 0.693/k$

in Table -1.

Corrosion in acid: The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 365.2, 1887.6, 3580.9 and 5205.2 mg/dm² in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 concentrations respectively for a period of 24 h at 301 ± 1 K as shown

Corrosion in presence of inhibitors: To assess their protective value aniline was added in 20, 40, 60 and 80 mM concentration in 0.01, 0.05, 0.10 and 0.15 M H₃PO₄ acid concentrations for 24 h duration period (Table -1).

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the aniline increases with the inhibitor concentration, e.g. in case of aniline in 0.01 M H_3PO_4 the I.E. was found to be 90.7, 94.7, 96.0 and 98.7 % with respect to 20, 40, 60 and 80 mM inhibitor concentration respectively [Table -1].

Effect of acid concentration: At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At 80 mM inhibitor concentration, the I.E. of aniline is 98.7, 94.1, 80.3 and 54.5 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively [Table -1].

		Acid concentration							
System	Inhibitor	0.01 M		0.05 M		0.10 M		0.15 M	
	Concentration	CR	I.E.	CR	I.E.	CR	I.E.	CR	I.E.
	mM	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%
А		365.2	-	1887.6	-	3580.9	-	5205.2	-
В	20	34.1	90.7	1163.7	38.3	2473.6	30.9	4168.1	19.9
	40	19.5	94.7	579.4	69.3	1864.9	47.9	3705.5	28.8
	60	14.6	96.0	219.1	88.9	1197.8	66.5	3028.7	41.8
-	80	4.9	98.7	112.0	94.1	706.0	80.3	2366.5	54.5
A = H	H ₃ PO ₄	B =	$B = H_3PO_4 + aniline$						

Table – 1 Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 acid containing aniline as inhibitor for an immersion period of 24 h at 301 ± 1 K.

Table - 2 Effect of temperature on corrosion rate (CR), inhibitive efficiency (I.E %.), energy of
activation (E a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG°_{a}) for zinc in 0.05 M
H ₃ PO ₄ acid containing inhibitor.

Inhibitor concentration = 80 mM Immersion period = 3 h						-3h Effe	Effective area of specimen = 0.2053 dm^2						
Temperature, K									Mean	Ea			
										From			
	303 313		3	323		333		From	Arrheni	Q _{abs}	(kJ mol	l ⁻¹)	
										us			
System	CR	I.E.	CR	I.E.	CR	I.E.	CR	I.E.	Eq(1)	Plot	303-	313-	323-
											313	323	333
	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%	kJ mol ⁻¹	kJ mol ⁻¹			
А	832.6	-	993.3	-	1193.0	-	1314.7	-	12.7	15.3	-	-	-
В	14.6	98.2	19.5	98.0	29.2	97.6	34.1	97.4	23.5	23.4	-9.1	-18.7	-5.5
$A = H_2 P \Omega_4$ $B = H_2 P \Omega_4 + aniline$													

 $A = H_3PO_4$ в = H₃PO₄ + aniline

Table-3 Polarisation data and inhibition efficiency (I.E.) of anilines for zinc in 0.01 M H₃PO₄ at 301 ± 1 K.

Inhibitor	concentratio	n: 80 mM	Effective area of specimen = 0.0268 dm^2							
		CD	Tafel slope	(mV/decade)	I.E. (%) from methods					
System	E _{corr} mV	I_{corr} mA/cm ²	Anodic	Cathodic	В	Weight	By			
					(mV)	loss	polarization			
			β_a	-β _c						
А	-940	0.560	88	117	22	-	-			
В	-920	0.005	280	130	39	98.7	99.1			
$A = H_2 P O_4$		$B = H_2 P O_4$	+ aniline							

 $A = H_3 PO_4 \qquad B = H_3 PO_4 + aniline$ $\beta_{a=} Anodic Tafel constant, \qquad \beta_C = Cathodic Tafel constant.$

CD = Corrosion current density from interception of anodic and cathodic lines.

Effect of temperature: Table-2 shows that as the temperature increases, corrosion rate increases while percentage of I.E. decreases. Mean 'Ea' values were calculated by using eq.2 for zinc in 0.05 M H₃PO₄ is 12.7 kJmol⁻¹ while in acid containing inhibitor, the mean Ea values are found to be higher than that of uninhibited system. The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface¹². The values of Ea calculated from the slope of Arrhenius plot (Fig.2) and using eq.2 are almost similar. From Table 2, it is evident that in all cases, the Q_{ads} values are negative and ranging from -5.5 to -18.7 kJmol⁻¹. The mean Δ Ga values are negative almost in all cases and lie in the range of -21.6 (20 mM) to -27.3 kJmol⁻¹ (80 mM). This suggests that they are strongly adsorbed on the metal surface. This statement

was supported by the work of Talati and Darji¹³. The enthalpy changes (ΔH_a) are positive (20.9 kJmol⁻¹) indicating the endothermic nature of the reaction¹⁴ suggesting that higher temperature favours the corrosion process. The entropy (ΔS_a) values are positive (0.15 kJmol⁻¹) confirming that the corrosion process is entropically favourable¹⁵.

Polarization behaviour: Anodic and cathodic galvenostatic polarization curve shown in Fig.3 indicates polarisation of both anodes as well as cathodes. The I.E. calculated from Tafel s plots agree well (within ± 1 %) with the values obtained from weight loss data (Table-3).



Fig. 1: Plot of log (θ /1- θ) versus log C for inhibitors in 0.01 M phosphoric acid concentration



Fig. 2: Arrhenius plots for corrosion of zinc in 0.05 M phosphoric acid in presence of 80 mM inhibitor concentration



Fig. 3: Polarisation curves for corrosion of zinc in 0.01 M phosphoric acid containing without and with 80 mM aniline as inhibitor.

Mechanism of corrosion inhibitor: Generally, zinc dissolve in phosphoric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn -----> Zn^{+2} + 2e^{-}$$
 (anodic reaction)
-----(7)

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

 $2H^{+} + 2e^{-} ----> 2H_{(ads.)}$ (cathodic reaction)

or $H + H_3O^+ + e^- - H_2\uparrow + H_2O$

The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when log (θ /1- θ) is plotted against log C straight lines are obtained in the case of inhibitor used (Fig.1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

Aniline is a weaker base than the primary aliphatic amines due to resonance, which is not possible in aliphatic amines.



Due to resonance, in aniline the l.p. of electrons on the nitrogen atom is less available for coordination with a proton than that in aliphatic amines where the phenomenon of resonance is not possible. In addition to this, the small positive charge on the N-atom in aniline due to resonance tends to repel the proton. Thus, aniline becomes less basic.¹⁶ Aniline on accepting a proton may give a small concentration of the cation C_6H_5 +NH₃ (onium) which does not show resonance. As there is more resonating structures possible for aniline than for onium ion, the former will be stabilized with respect to the latter.¹⁷

It appears that nitrogen atom of amino group (- NH_2) in aniline acts as the reaction centre (polar function) because of its higher electron density. This reaction centre forms a monolayer on the zinc surface. Moreover, aniline assumes a small positive charge in acid solutions due to protonation of amino (- NH_2) group, higher electron density of the nitrogen atom facilitates the protonation. As the concentration increases the rate of protonation also increases. The

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successive increase in protonation may be responsible, in many cases, for the enhancement of the I.E.

<u>Conclusion</u>

*As the acid concentration increases the corrosion rate increases.

*At constant inhibitor concentration, the I.E. of all inhibitors decreases as the concentration of acid increases.

*At all concentration of acid, as the inhibitor concentration increases I.E. increases and corrosion rate decreases.

*Addition of inhibitor in corrosive media indicates that as the temperature increases corrosion rate increases while I. E. decreases.

Acknowledgement:

The authors are thankful to Department of Chemistry, Navyug Science College, Surat for providing laboratory facilities.

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